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Casimir Effect In Quantum Physics

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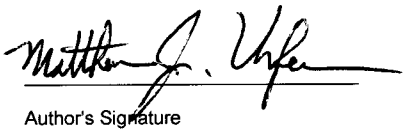

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The Casimir Effect in Quantum Physics

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Matthew James Urfer

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The Casimir Effect in Quantum Physics

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Abstract

The Casimir Effect while over 60 years old, still holds profound implications for several branches of Physics, including but not limited too, Quantum Field Theory, Mathematical Physics, and Cosmology. This paper offers a review of Casimir Physics in regard to Quantum Physics.

Dedications

I wish to dedicate this thesis to my Mom and Dad, Jim and Susan Urfer.

For without their love and support this work would have never have been possible.

Acknowledgements

I wish to thank my thesis advisor, Dr. Patrick Coulton, for his patience and counsel. I also wish to thank Eastern Illinois University.

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Section 1. Introduction

In the late 19th and early 20th century classical physics was undergoing a renaissance. Classical physics had made great strides in its development, but scientists still could not explain certain phenomena. One such subject was the radiation process of a black body. In 1900 the work of a German physicist, Max Planck, led to the development of a new theory of physics that would supplement the theories of classical physics.

Dissatisfied with classical mechanics' obvious deficiency with regard to black body radiation, Planck set out to improve on the classical model. Planck hypothesized that the radiant energy that the black body released and absorbed could be quantized into packets of energy which Planck denoted as *quanta*. This radical hypothesis became the starting point of new physics that would be known as quantum physics. While much of quantum physics agrees with classical physics, quantum physics also produced interesting anomalies.

In classical physics, it was thought that when the temperature of an object reached absolute zero that all motion, including atomic and molecular motions, should cease. In other words, the kinetic energy of the object in question should be reduced to zero as the temperature approached absolute zero. However, something completely different and unexpected resulted from Planck's analysis. Planck found that as an object approached absolute zero, the energy of the object approached a constant value that was not zero.

Enter one of era's greatest minds, A. Einstein. In 1913, Einstein picked up where Planck had left off. Einstein refined Planck's distribution law and found what he later called the zero point energy of the system, which is dependent only on the energy at temperature zero. The zero point energy term then sat in obscurity until a brilliant physicist, H.B.G. Casimir, showed how important this obscure term would be to understanding physics.

Casimir found that the zero point energy was much more than a leftover term on a distribution law. He discovered that the zero point energy would be important in finding an intrinsic force on conducting parallel plates. Thus the Casimir effect was born.

Section 2. Old Quantum Mechanics

According to classical electromagnetic theory, the spectral distribution of energy in a black body with ideal emissivity ought to satisfy the Rayleigh-Jeans distribution curve.

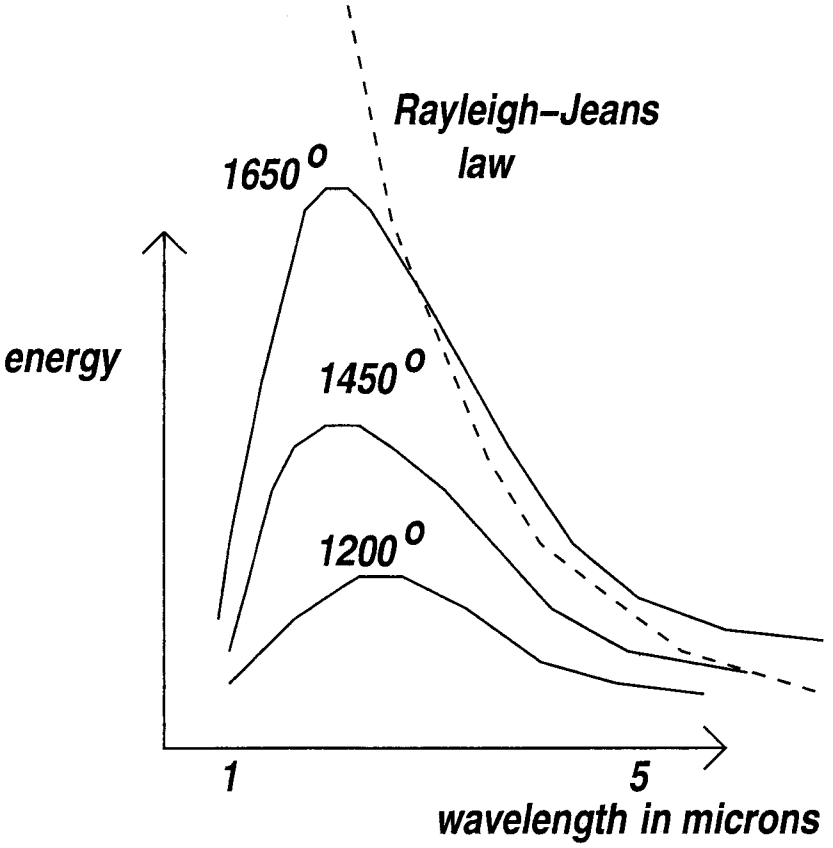

Figure 1. *Black body wavelength output for various temperatures.*

The Rayleigh-Jeans formula predicts that the radiation intensity should vary as the inverse fourth power of the wavelength. But this is not observed. The prediction appears to be a good fit for the long wavelength portion of the spectrum, but it is clearly incorrect for the short wavelength portion of the spectrum (Fig. 1).

This anomaly in classical theory led Max Planck to consider the possibility that energy-wavelength spectrum emitted from the black body was not a continuous spectrum. Hence, he assumed that the energy was emitted in a certain discrete set of wavelengths. Starting with this assumption, Planck imagined that the black body was composed of a finite set of harmonic oscillators. If one assumes that the energy is proportional to the frequency, then each oscillator X_i will emit energy

$$U_i = h_i \nu_i,$$

for some proportionality constant h_i, provided that the harmonic oscillators are of the same type with possibly varying frequencies. Planck showed that as h_i tends to zero, the spectral distribution tends to the Rayleigh-Jeans distribution. From this point of view, it becomes clear why the continuous energy distribution assumption might make a good fit for larger wavelength (or low frequency) emitters.

On the other hand, allowing h_i to tend to zero would imply that there should be nearly infinitely many oscillators with very small energy outputs. This result contradicts well known empirical observations at short wavelengths. Hence, it was thought that $h_i = h$ ought to be a constant for all oscillators of this type.

Of course, it is now well known that these oscillations are due to molecular vibrations and electron shell transformations about the nucleus of an atom and that there are only certain allowed oscillations and the variations in the energy levels. All such radiation producing oscillations are ultimately related to the universal constant h, also known as Planck's constant.

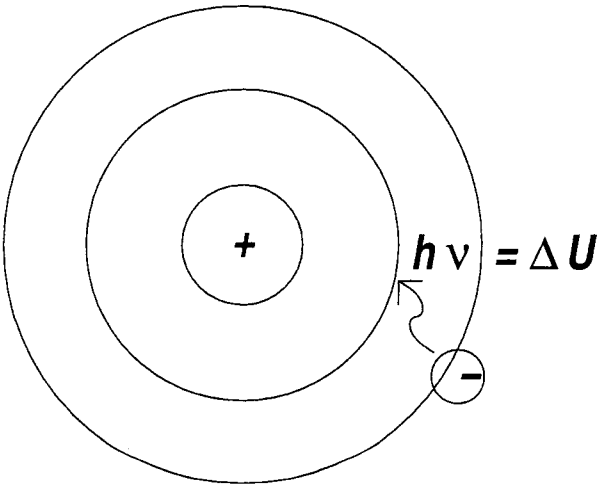

Figure 2. *The idealized atomic model.*

The correspondence principle was postulated by Neils Bohr, while he was working on his theory of atomic structure. It states that as the physics of a system at submicroscopic, or quantum, level approaches the macroscopic level, then the physics of the quantum level system must be in complete agreement with established classical physics. The modern equivalent of this principle in quantum mechanics dictates that as the quantum numbers of a system get exceedingly large, the physical model of the quantum level system must agree with the classical physics model of the same system. If the correspondence principle did not

hold, we would be forced to conclude that quantum theory did not agree with the empirical observation on which classical theory is based.

An excellent example of the correspondence principle is supplied by Bohr's model of a hydrogen atom. Consider the frequency of the photon emitted in transition from an initial energy level n to a final energy level $n-1$. Applying the principles of quantum physics, the frequency can be expressed by the relation

$$f = \frac{c}{\lambda} = \frac{2\pi^2 Z^2 m\kappa^2 e^4}{R^3}\left[\frac{1}{(n-1)^2} - \frac{1}{n^2}\right] = \frac{2\pi^2 Z^2 m\kappa^2 e^4}{R^3}\frac{2n-1}{n^2(n-1)^2},$$

where m is the mass of the hydrogen atom, κ is Boltzmann's constant, e is the charge on the electron, Z is the number of electrons of the atom, and here n is the quantum number of the system. As n gets exceeding large, we have that $(2n-1)/n^2(n^2-1)$ approaches $2/n^3$. Thus the frequency of the system is approximated by

$$f \approx \frac{4\pi^2 Z^2 m\kappa^2 e^4}{R^3 n^3}.$$

The classical solution of the system is straight forward. Since the classical frequency is defined as

$$f = \frac{\nu}{2\pi r}, \text{ with } \nu = \frac{nh}{2\pi mr}, \text{ and } r = \frac{n^2 R^2}{4\pi^2 m\kappa Z e^2}.$$

we can combine the relations to obtain

$$f = \frac{nh}{4\pi^2 mr^2} = \frac{nh}{4\pi^2 m\left(n^2R^2/4\pi^2 m\kappa Z e^2\right)^2} = \frac{4\pi^2 m^2\kappa^2 Z^2 e^4 nh}{mn^4\hbar^4} = \frac{4\pi^2 Z^2 mk^2 e^4}{R^3 n^3}.$$

Consequently, the classical calculation of the frequency agrees with the quantum mechanics calculation of the frequency in the limit of increasing quantum number n (cf. [9]).

Section 3. Applications of Quantum Theory

A black body consists of an enclosure that is at a uniform absolute temperature (hereafter referred to as temperature), T, which absorbs all the radiation energy that contacts its surface.

If a small hole were made in the wall of the black body the radiation emitted from the black body via the hole would only depend on the temperature of the black body. Thus the radiation energy density, u, is a function only of the temperature T.

Since the black body has a uniform temperature T, the radiation energy inside the black body is assumed to be isotropic. According to the classical theory of electromagnetism, the isotropic radiation energy in the black body exerts a uniform pressure, P, on the walls of the black body. The value of this pressure equates to a third of the energy density of the black body. This means that

$$P = \frac{u}{3},$$

where the energy density, and hence the pressure, is dependent only on the temperature of the black body. The radiation energy density u, can therefore be expressed as the total energy of the black body, U, over the volume, V, of the black body. Consequently, the total energy of the system is $U = uV$.

Applying an equation derived from the first and second law of thermodynamics, and assuming that T and V are independent, we obtain

$$\frac{\partial U}{\partial V} = T\frac{\partial P}{\partial T} - P.$$

Now the radiation energy density u as a function of T can be derived as follows [7]. Since $U = uV$, then

$$\frac{\partial U}{\partial V} = u.$$

Furthermore,

$$\frac{\partial P}{\partial T} = \frac{1}{3}\frac{\partial u}{\partial T} = \frac{1}{3}\frac{\partial u}{\partial T},$$

since P and u depend only on T. Substituting these equations in for the their respective partial derivatives yields,

$$u = \frac{\partial U}{\partial V} = T\frac{\partial P}{\partial T} - P = \frac{1}{3}T\frac{du}{dT} - \frac{1}{3}u.$$

Solving for u gives

$$u = \frac{T}{4}\frac{du}{dT},$$

which in turn implies that

$$u = \sigma T^4,$$

where σ is the constant of integration.

The value of σ is $7.561 \times 10^{-16}\mathrm{Jm}^{-3}\mathrm{s}^{-1}\mathrm{K}^{-4}$ (i.e., Joules per cubic meter seconds times Kelvin degrees to the fourth power) and is known as the Stefan-Boltzmann constant . While a black body can be treated classically, it is also necessary to consider it from the point of view of quantum mechanics.

Using the original definition of a black body it is possible to derive the radiation energy density, u, in terms of the temperature, T, of the black body. To do this, consider the original black body, except this time let the isotropic radiant energy consist of quanta, or packets of radiant energy known as photons. This was Planck's hypothesis when he begin looking for a way to explain the distribution of the radiant energy inside the black body.

From the perspective of quantization, we see that the black body essentially becomes an isotropic distribution of photon gas. Since the photons are indistinguishable, due in part to the isotropic nature of the problem, the radiant energy in the black body is assumed to behave according to Bose-Einstein statistics. To that end, the number of photons in the black body is a dependent variable and thus the total number of photons in the black body is given by the reduced Bose-Einstein distribution function,

$$\Delta\mathcal{N}_\nu = \frac{\Delta\mathcal{G}_\nu}{\exp(h\nu/\kappa T) - 1},$$

where ν is the frequency of the photons and $\Delta\mathcal{G}_\nu$ represents the degeneracy of the system. This distribution function represents the total number of stationary waves in the system, in this case the black body, over the frequency interval $[\nu, \nu + \Delta\nu]$. In general, the number of stationary waves in a system with a fixed frequency ν is given by

$$\mathcal{G}_1 = \frac{4\pi}{3}\frac{V}{c^3}\nu^3.$$

Due to the transverse nature of electric field in an electromagnetic waves, it is necessary to consider the two linearly independent opposing waves contributing to a given stationary wave. Thus the volume of stationary waves as given above must be doubled. Hence, the previous formula is refined to

$$\mathcal{G}_2 = \frac{8\pi}{3}\frac{V}{c^3}\nu^3.$$

Now the degeneracy formula can be readily obtained

$$\Delta \mathcal{G}_\nu = \frac{8\pi V}{c^3}\nu^2 \Delta\nu.$$

Substituting this into distribution function, $\Delta \mathcal{N}_\nu$, determines the number of photons in the black body:

$$\Delta \mathcal{N}_\nu = \frac{8\pi V}{c^3}\frac{\nu^2}{\exp(h\nu/\kappa T) - 1}\Delta\nu.$$

Since the energy density of each wave of the black body is given by,

$$\frac{U}{V} = h\nu,$$

we have that the energy density of all the photons in the system is defined as

$$\Delta u_\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{\exp(h\nu/\kappa T) - 1}\Delta\nu,$$

which is known as the spectral energy density and is analogous to the energy density, u, of the classical system. This is known as Planck's distribution law.

Its worth noting that at a specific temperature, T, where the frequency of the photons is high enough such that $h\nu >> kT$, it is clear that the exponential term for the spectral energy density becomes large enough to ignore the other term in the denominator and we obtain that the distribution approximately follows Wein's distribution law, or

$$\Delta u_\nu \approx \frac{8\pi h}{c^3}\frac{\nu^3}{\exp(h\nu/\kappa T)}\Delta\nu.$$

Similarly at a specific temperature, T, where the frequency of the photons is low enough such that $h\nu << kT$, we obtain that $[\exp(h\nu/\kappa T) - 1] \approx h\nu/\kappa T$ and the spectral energy density approximates the Rayleigh-Jeans distribution law, or

$$\Delta u_\nu \approx \frac{8\pi\kappa T}{c^3}\nu^2 \Delta\nu.$$

This relationship between the distribution laws of Planck, Wein and Rayleigh-Jeans is easily seen in the in Figure 3 below. Now the total energy of the black body can be derived by integrating Planck's distribution over all frequencies in the interval $[0, \infty]$,

$$u_\nu = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3}{\exp(h\nu/\kappa T) - 1}d\nu$$

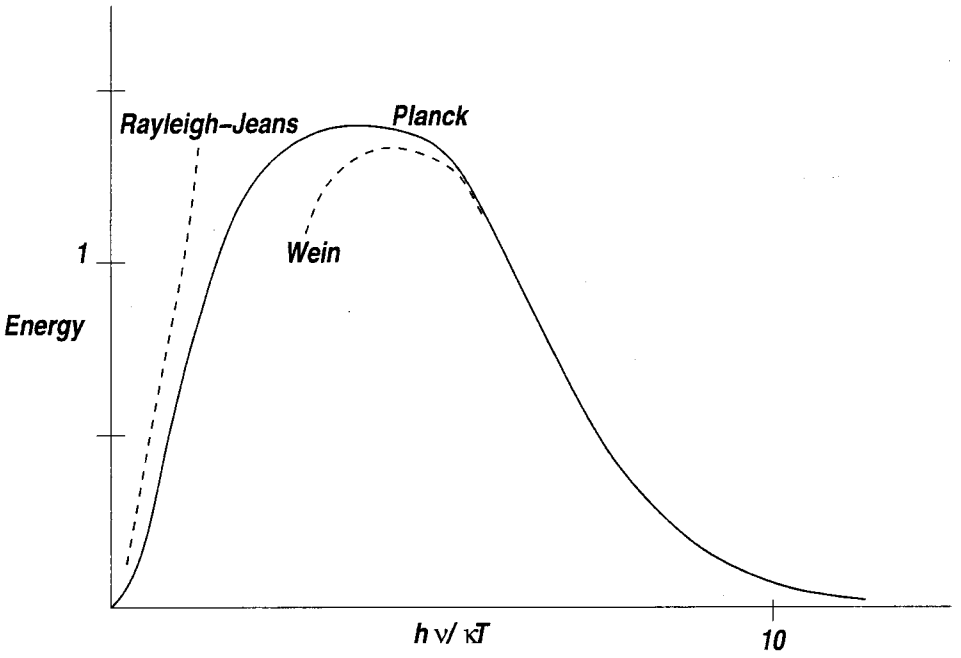

Figure 3. The Planck distribution.

If we let $x = h\nu/\kappa T$, then $d\nu = (\kappa T/h)dx$ and the integral becomes

$$u_\nu = \frac{8\pi h}{c^3}\int_0^\infty \frac{(\kappa T x/h)^3}{\exp([h(\kappa T x/h]/\kappa T) - 1}\frac{\kappa T dx}{h} = \frac{8\pi\kappa^4}{c^3R^3}T^4\int_0^\infty \frac{x^3}{e^x - 1}dx.$$

In particular,

$$\int_0^\infty \frac{x^n}{e^x - 1}dx = n!\zeta(n+1)$$

where $\zeta(n)$ is the Riemann zeta function. Evaluating the integral gives the result $\pi^4/15$. Now we obtain the familiar formula,

$$u_\nu = \frac{8\pi^5\kappa^4}{15c^3R^3}T^4 = \sigma T^4,$$

where σ is the Stefan-Boltzman constant (cf. [8]).

Another phenomenon that did not yield to a classical explanation involved the property of metals which emit electrons when bombarded by high energy radiation. This is the well known photo-electric effect. Scientists observed that when the frequency of the radiation was reduced below a critical, or threshold value, the metal would no longer emit electrons. According to classical theory, as the frequency is reduced, the metal should continue to emit electrons since it is assumed that electrons are bound at all energy levels.

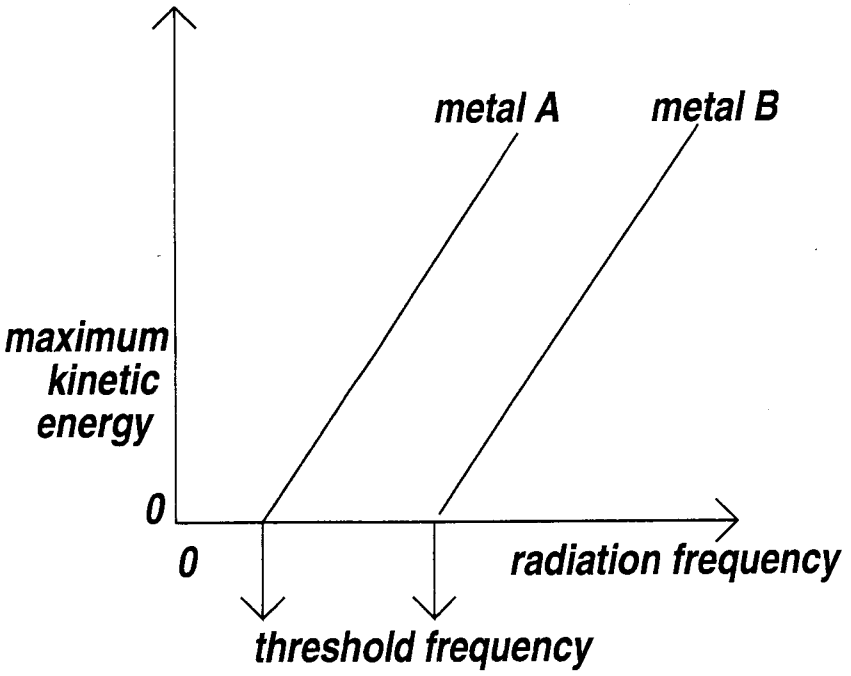

Figure 4. *Energy independent of light intensity, depends only on frequency/energy.*

A young Swiss patent clerk by the name of Albert Einstein considered whether Planck's new theory might apply to the problem of electron emission from these metals. Assuming that the binding energies for electrons in the metal were given by discrete energy levels of the form $h\nu$ which would mean that energy would also be absorbed in discrete amounts. From this, Einstein was able to see that there must be a minimum binding energy and that this threshold, frequency/energy would be dependent on the particular metal. Empirical observation showed that the threshold energies for various metals were multiples of Planck's constant.

Once again, the correct explanation is that the electrons that are most loosely bound to the atoms in the metal are bound at specific energies associated to the outer electron shells. In order to knock an electron out of its shell it is necessary for the energy of the radiation, $U = h\nu$, to be high enough to impart sufficient momentum to the electron so that it may overcome this binding energy. As we now know, the binding energies are quantized according to Planck's original assumption.

This in itself does not lead directly to the theory of quantum mechanics. The quantization of solutions to differential equations is a well known phenomena. In particular, such quantization occurs in the wave equation for a fixed string.

Consider the solutions of the wave equation using separation of variables on a string of

fixed length $L = \pi$

$$v^2 \frac{\partial^2 u(x,t)}{\partial x^2} = \frac{\partial^2 u(x,t)}{\partial t^2}$$

$$u(0,t) = 0,\ u(\pi,t) = 0, \forall t,\ \text{and}\ u(x,0) = f(x),$$

where $v = 1$ is a constant associated to the speed of the wave. For $u = X(x)W(t)$ we have

$$\frac{d^2X}{dx^2} = -\frac{\lambda^2}{v^2}X,\ \text{and}\ \frac{d^2W}{dt^2} = -\lambda^2 W.$$

The initial condition on the node positions of the string implies that there is a set of quantized separation constants exhibiting the values $\lambda_n \in \mathbf{Z}^+$. This in conjunction with the initial conditions gives a set of basic solution types

$$W_n(t) = A_n \sin(vnt) + B_n \cos(vnt)\ \text{and}\ X_n(x) = C_n \sin(nx)$$

which in turn gives a Fourier basis for a complete solution:

$$u(x,t) = \sum_{n=1}^{\infty} C_n \sin(nx)\cos(vnt),\ \text{where}\ f(x) = \sum_{n=1}^{\infty} C_n \sin(nx)$$

is the Fourier representation of the initial position height function $f(x)$.

We note that the possible modes of vibration are quantized by the harmonics of the string parameterized by n.

Yet there was even earlier evidence of the quantized nature of electron energy levels in the structure of the atom. Many scientists performed experiments on hydrogen and other gas combinations by running an electric current inside a glass tube filled with gas. It was well known that when a sufficiently high voltage was placed across the tube that a current was produced and the current caused the gas inside the bulb to give off a light.

Different gasses produced distinguishable colors and the colors emitted by the bulbs could be easily separated using a prism. The prism separation technique disclosed the fact that the light spectrum was not anything like continuous. In fact, it was observed that the hydrogen gas spectrum produced exactly four visible colors with the corresponding visible wavelengths ranging from about 410 nanometers to about 656 nanometers.

It is now known that the electron beam in the electric current collides with electrons sitting in the stable energy shells of the hydrogen atom. The electron collisions may cause a bound electron to be excited into a higher energy level, which is quantized as we have seen. The electron will, according to some stochastic process, then seek a lower energy level

in the atom. As the electron falls into a lower stable energy shell it loses energy and gives off light with a characteristic frequency determined by a multiple of Planck's constant.

In 1885 (about 15 years before Planck's discovery), Johann Balmer observed that the spectrum had the form of a sequence. To see how he might have approached this problem, consider the hydrogen wavelength partial sequence in nanometers

$$\{410, 434, 486, 656\}$$

with

$$\frac{656}{486} \approx 1.34, \frac{486}{434} \approx 1.19, \text{ and } \frac{434}{410} \approx 1.06.$$

Figure 5. *A representation of the Balmers series.*

Now observe that

$$\frac{n^2}{n^2-4} \to \{\frac{9}{5}, \frac{16}{12}, \frac{25}{21}, \frac{36}{32}\} \approx \{1.8, 1.33, 1.19, 1.12\}, \text{ for } n = 3, 4, 5, 6.$$

We may estimate an idealized limiting wavelength (i.e. the limiting wavelength as the quotient $n^2/(n^2-4) \to 1$) by

$$656.1 \times \frac{5}{9} \approx 364.5.$$

Now we have the following relations:

$$364.5 \times \frac{9}{5} \approx 656; \; 364.5 \times \frac{16}{12} \approx 486;$$

$$364.5 \times \frac{25}{21} \approx 434; \; 364.5 \times \frac{36}{32} \approx 410.$$

Perhaps it is not so surprising that Balmer was able to obtain a sequence formulation for the visible spectrum of light emissions from the hydrogen atom. What is more surprising is that the theory worked well for all known atomic emission spectra.

Classical mechanics begins with Isaac Newton's demonstration of Kepler's laws by the application of theoretical techniques. In particular, Newton showed that the inverse square central force law for gravitational attraction implies that for one fixed planet and one orbiting planet the orbits are ellipses.

J.J. Thomson, who discovered the electron using the fact that the attractive inverse square law applies to oppositely charged bodies, hypothesized that electron orbits of the hydrogen atom would take the effective form of the harmonic oscillator solutions, while at the same time realizing that such an electron would undergo continuous acceleration. Accelerating charged particles, according to classical principles, will typically produce radiation which in turn draw energy away from the charged particle. Thus a charged particle orbiting about a fixed nucleus would continuously lose energy and be drawn into the nucleus.

In order to avoid this catastrophic conclusion, Thomson proposed, in 1904, that the electrons with negative charge in an atom ought to be stationary in a soup, or cloud of positive charge. This is sometimes referred to as the Plum Pudding model of the atom.

The proposed model required further study into the basic structure of the atom. Hans Geiger and Ernest Marsden conducted a series of experiments wherein thin metal foils were bombarded by positively charged alpha particles. Most notable among these was the study of gold foil. In as much as gold has a very high atomic number, it provides a solid and virtually immovable atomic particle for the experiment. Ernest Rutherford, in 1911, interpreted the empirical result of the experiment to indicate that the beam of alpha particles aimed at the gold foil were deflected as would be expected if one assumed a repulsive central inverse square law and a very compact nucleus.

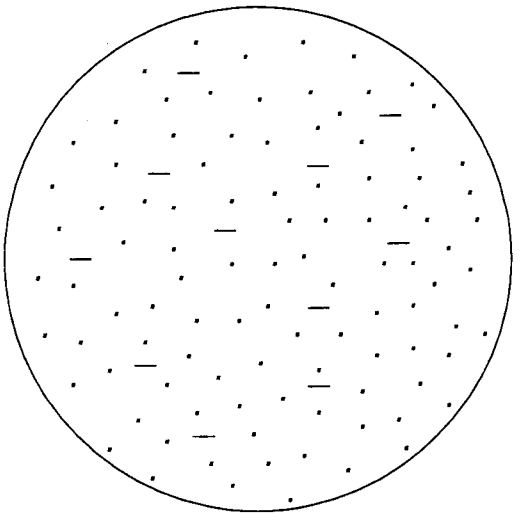

Figure 6. *The Plum Pudding model with static negative charges.*

This interpretation cast the Thompson model into doubt and implied a reversal of the form the model should take. In other words, it appeared that the positive charge was fixed

and stable in a central nucleus and that the negative charges (though they were known to have a particle nature) were somehow arranged in a cloud-like mist.

Of course, this solution was not particularly satisfying in as much as there still was no explanation of the nature of the orbiting electrons with respect to their properties of acceleration about the nucleus and the light spectra which the various atoms produced.

In 1913, Niels Bohr attempted to explain the quantum nature of the hydrogen atom making use of the advances by Thomson and Rutherford. The Bohr model treats the atom with a small nucleus and a series of possible electron orbits whose energy differs by some multiple of Planck's constant, i.e., $\Delta U = h\nu$.

According to Bohr's model, when the electron moves from a higher energy shell to a lower energy shell with energy difference ΔU, it emits radiation with energy $\Delta U = h\nu$, where ν is the frequency of the emitted radiation. In this concept of the atom, a change in shell binding energy causes spectral radiation rather than a change due to acceleration.

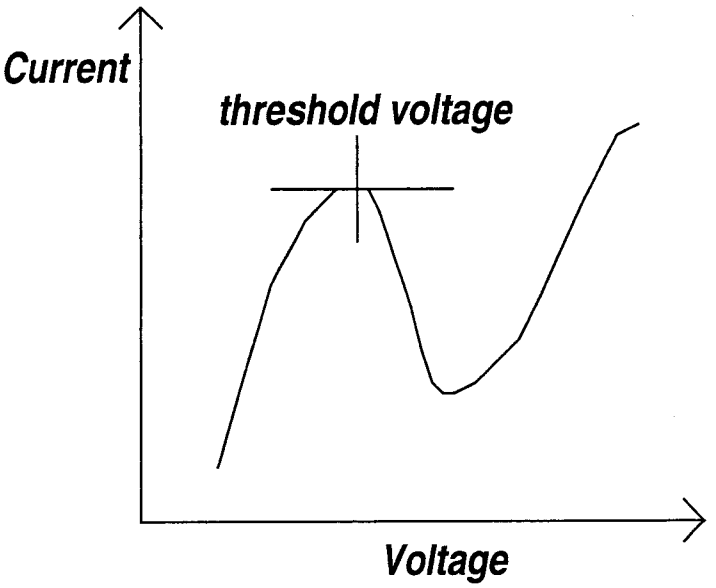

Figure 7. *The current-voltage relation in the Franck-Hertz experiment.*

In 1914, J. Franck and G. L. Hertz conducted an experiment to test the energy orbital properties of electron shells for the mercury atom. Franck and Hertz constructed a tube with mercury vapor which could conduct a current. Since they knew the lowest energy level at which the mercury vapor would produce spectral radiation, they deduced that any electron striking a mercury atom at a low energy level would have an essentially elastic

collision.

To test this theory, they placed a grid in the middle of the tube which would catch electrons whose initial energy levels had been significantly reduced by inelastic collisions. Franck and Hertz observed that as the voltage increased below the threshold level the current increased according to the usual theory of a small resistance in the circuit. When the voltage hit the threshold energy, the mercury atom began to emit the characteristic radiation associated to the electron energy level in the current. Simultaneously, the current to the anode dropped precipitously indicating that several electrons had undergone inelastic collisions so that they were then captured by the intervening grid. The experiment verified the energy configuration model of Bohr's atom.

Section 4. The Theory of Quantum Mechanics

The Bohr model is unsatisfactory in the sense that it proposes a theory based on known empirical data without a mathematically consistent theory which could be used to make predictions. The success of the Bohr model is found in its ability to join the empirical data into a coherent theory. The race was on to find a theory that clarified the nature of the Bohr model.

The next decade of research involved attempts to find an theoretical answer to the problem of the Bohr model. Many of these attempts involved a marriage of classical and quantum techniques. Recall that the energy or action integral along a particle path is given by the classical formula

$$\Delta U = \int_o^{v_f} mvdv = \int_o^T mr'(t)\frac{dr'}{dt}dt$$

As an electron moves from a one energy state in the atom to another energy state it is supposed that the energy integral satisfies the classical formula. It is then hypothesized that, in transition between states, the particle undergoes a characteristic oscillatory motion which produces the associated radiation. But once again this is an attempt to make the classical theory adjust to the Bohr model. Considering the solution of the wave equation, the quantized coefficients in the integral are then identified with the Fourier coefficients in the wave equation.

In 1925, Werner Heisenberg considered the case of the harmonic oscillator with form

$$r_\Delta(t) = r_\Delta(0)\ \exp(i\frac{\Delta U}{h}2\pi t).$$

From this point of view, we can see that Heisenberg begins by assuming a solution which takes the form of an harmonic oscillator and from this obtains a relation between the momentum and position operators that determine the quantization properties of the atomic structure. Max Born recognized the Heisenberg formulation as a matrix product and along with P. Jordan developed the matrix operator theory version of quantum mechanics.

On the other hand, inspired by the work of H. Weyl, Erwin Schroedinger, using energy considerations and the Euler-Lagrange variational technique, produced a partial differential equation for the central force problem with two separation constants. In this case, the solution of the equatorial form of the separated partial differential equation was given by the solution of the harmonic oscillator and the quantization numbers were determined by

the separation constants along with the initial constraints in much the same way as in the wave equation.

We begin our consideration of the harmonic oscillator in quantum mechanics with the remark that the differential equation

$$x\frac{d}{dx}\cdot\psi(x)-\frac{d}{dx}x\cdot\psi(x)=-\psi(x)$$

is satisfied for all functions $\psi(x)$. We seek to rewrite the relation as an operator relation. We define the function operators $I(\psi(x))=\psi(x)$, $X(\psi(x))=x\cdot\psi(x)$ and $D(\psi(x))=\psi'(x)$. This implies that the differential operator

$$XD-DX=-I.$$

Now we define a momentum operator by

$$P(\psi(x))=-\frac{ih}{2\pi}D(\psi(x)).$$

The classical Hamiltonian for the one dimensional harmonic oscillator is given by

$$\frac{p^2}{2m}+\frac{m\omega^2}{2}x^2=U,$$

where we have written $\omega=\alpha/\sqrt{m}$ replacing the spring constant given by the spring force relation $F=-\alpha^2x$. Applying operator theory to the Hamiltonian gives

$$\Big[-\frac{h^2}{8\pi^2m}D^2+\frac{m\omega^2}{2}X^2\Big]\psi(x)=U\cdot\psi(x),$$

or,

$$\Big[D^2+(\eta I-\mu^2X^2)\Big]\psi(x)=0,\ \text{where}\ \mu=\frac{2\pi\omega m}{h}$$

and $\eta=8\pi^2mU/h^2$.

To simplify the problem it is assumed that the function $\psi(x)$ is normalized (i.e., $\psi(x)$ is a unit vector in an appropriate Hilbert space). As a first step, we consider a possible solution of the form $\psi(x)=\exp(-\mu x^2/2)$ and compute

$$\Big[D^2-\mu^2X^2\Big]\psi(x)=\frac{d}{dx}[-\mu x\exp(-\mu x^2/2)]-\mu^2x^2\exp(-\mu x^2/2)=$$

$$-\mu\exp(-\mu x^2/2)+\mu^2x^2\exp(-\mu x^2/2)-\mu^2x^2\exp(-\mu x^2/2)$$

$$=-\mu\exp(-\mu x^2/2).$$

Thus $\exp(-\mu x^2/2)$ is an eigenfunction when $\mu = \eta$, or

$$U_o = \frac{h\omega}{4\pi},$$

which gives the zero point energy.

Zero point energy as a concept was developed by Albert Einstein and his assistant Otto Stern in 1913. Essentially the idea of zero point energy is that all oscillators, i.e., Planck's idea of quanta, still have some residual energy at absolute zero, or $0°K$. Einstein and Stern coined the German word *nullpunktsenergie* to describe their discovery, which is translated as zero point energy. After extensive analysis of the specific heat of hydrogen gas at low temperatures, they concluded that empirically the vibrational energy of an oscillator is

$$U = \frac{h\nu}{\exp(h\nu/\kappa T) - 1} + \frac{h\nu}{2}.$$

As the temperature approaches $T = 0°K$, the exponential term causes the denominator to approach ∞, thus causing the first term to approach 0. Hence, the term $h\nu/2$ is the zero point energy of the oscillator. Einstein and Otto remained unconvinced that the zero point energy term was equal to $h\nu/2$. However, in 1924 Mulliken showed that indeed the zero point energy was not only $h\nu/2$, but an integral part of quantum mechanics.

We let $f(x) = \exp(-\mu x^2/2)$ and generalize this solution to a form $y(x) = g(x)f(x)$ and obtain

$$\begin{aligned}\left[D^2 + (\eta I - \mu^2 X^2)\right] g(x)f(x) \\ &= [g''(x) - 2\mu x g'(x) + (\mu^2 x^2 - \mu)g(x) + \eta g(x) - \mu^2 x^2 g(x)]f(x) \\ &= 0.\end{aligned}$$

We have reduced the problem to Hermite's differential equation

$$g'' - 2\mu x g' + (\eta - \mu)g = 0.$$

Applying a power series technique gives the recursion formula

$$a_{n+2} = \frac{\eta - \mu(1+2n)}{(n+2)(n+1)} a_n.$$

If $\eta = \mu(2\ell + 1)$ for some $\ell \in \mathbf{Z}$, then the series truncates in a polynomial, i.e., a_n is only non-zero for $n = 0, ..., \ell - 1$. These are called the Hermite polynomials and they can be normalized to form an orthonormal basis for the solution space.

The quantization condition $\eta/\mu = 2\ell + 1$, implies that

$$U_\ell = (\ell + \frac{1}{2})\frac{h\omega}{2\pi}.$$

This quantization condition is essential for guaranteeing that the probability wave function $\Psi = g(x)f(x)$ has a bounded integral over the real line and so may be normalized for an appropriate choice of a_o.

As an example of the harmonic oscillator theory applied to the orbiting electron, we now consider the central force problem. The time independent Schroedinger equation takes the following form for the central force potential problem:

$$\frac{R^2}{8\pi^2 m}\nabla^2\psi(x,y,z) + \Big(E - V(r)\Big)\psi(x,y,z) = 0,$$

where the Hamiltonian is given by

$$H = \frac{p^2}{2m} + V(r)$$

for momentum operator p. The spherical coordinate form of Schroedinger's equation is given by

$$\Big(\frac{R^2}{8\pi^2 m}\Big[\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big) + \frac{1}{r^2\sin(\phi)}\frac{\partial}{\partial\phi}\Big(\sin(\phi)\frac{\partial}{\partial\phi}\Big) + \frac{1}{r^2\sin^2(\phi)}\frac{\partial^2}{\partial\theta^2}\Big] + E - V(r)\Big)\psi(r,\theta,\phi) = 0$$

We introduce two separation constants μ and β which lead to the following:

(a) the radial equation

$$\frac{h^2}{8\pi^2 m}\Big[\frac{1}{r^2}\frac{d}{dr}\Big(r^2\frac{d}{dr}\Big) + E - V(r) - \frac{\mu}{r^2}\Big]\mathbf{R}(r) = 0;$$

(b) the azimuthal equation

$$\Big[\frac{1}{\sin(\phi)}\frac{d}{d\phi}\Big(\sin(\phi)\frac{d}{d\phi}\Big) + \mu - \frac{\beta^2}{\sin^2(\phi)}\Big]\Phi(\phi) = 0,;$$

and (c) the equatorial equation

$$\Big[\frac{d^2}{d\theta^2} + \beta^2\Big]\Theta(\theta) = 0.$$

This last equation is the equation of the harmonic oscillator. A quantized value for $\beta = k \in \mathbf{Z}^+$ is determined by the condition that the solution is a periodic, or standing wave, and

the equatorial basic solution form $\Theta(\theta)$ is a probability density function. This quantization number determines the shell of the orbit.

The azimuthal equation reduces to Legendre's equation which implies that the basic solutions are Legendre polynomials, which means that the power series solutions are truncated to polynomials when $\mu = \ell(\ell+1)$ for $\ell \in \mathbf{Z}^+$. This is related to the so-called angular momentum quantum number.

Applying the quantum numbers to the radial equation we find that the radial equation is solved by a series of Legendre polynomials combined with exponential decay functions (cf. [10]).

5. The Theory of Intramolecular Bonding

The three recognized types of intra-molecular bonding, i.e, bonds which hold molecules together, are ionic bonding, covalent bonding and metallic bonding. For anintramolecular bonding to be stable it must generally be stronger than intermolecular bonds, The major forms of intermolecular bonding are generally referred to as the van der Waals forces and London dispersive forces.

Ionic bonding usually involves the interaction of the outer electron orbits between an atom classified as metallic and and an atom classified as nonmetallic. An ionic bond is formed when the electron clouds of two ionized atoms interact. One atom is positively ionized and called an anion when it is missing at least one electron in the outer shells. The other atom is negatively ionized and referred to as a cation when it possesses at least one extra electron in its outer shells.

Essentially the electron, or electrons, on the cation are attracted to the anion which draws the two atoms together. The electron cloud on the cation intersects with and becomes part of the cloud of the anion. It should be noted that while these electron clouds do intersect, the ionic bond is characterized by the fact that the atoms do not share any of their respective electrons. Shared electrons are called covalence electrons.

When two atoms of this kind come into close proximity, it is often the case that the outer electron of the metallic atom can fall into an orbit which is primarily surrounding the non-metallic atom. This is due to the reduction in energy for such an orbit. In particular, the outer electrons in a metallic structure are often loosely bound to the atom as a result that the outer electrons are shielded from the positive nucleus by many intervening shells of electrons.

This is important since the primary force that holds the two ions together is the electrostatic force between the cloud of the cation and its electrons interacting with the nucleus of the anion. This is, of course, known as Coulomb attraction. Metals are easily turned into cations due to the nature of a metallic atom's outer electrons being easily removed. Nonmetals will more readily gain electrons which causes them to become anions. Thus the ionic bond is usually formed between a metal and a nonmetal.

For example, if we consider the periodic table, each row in the table is referred to as a period. As the atomic number increases within a period, the atomic radius of the given elements decrease. This is due to the fact that the increase in positive nuclear charge forces

the electrons into shells that are more and more compact.

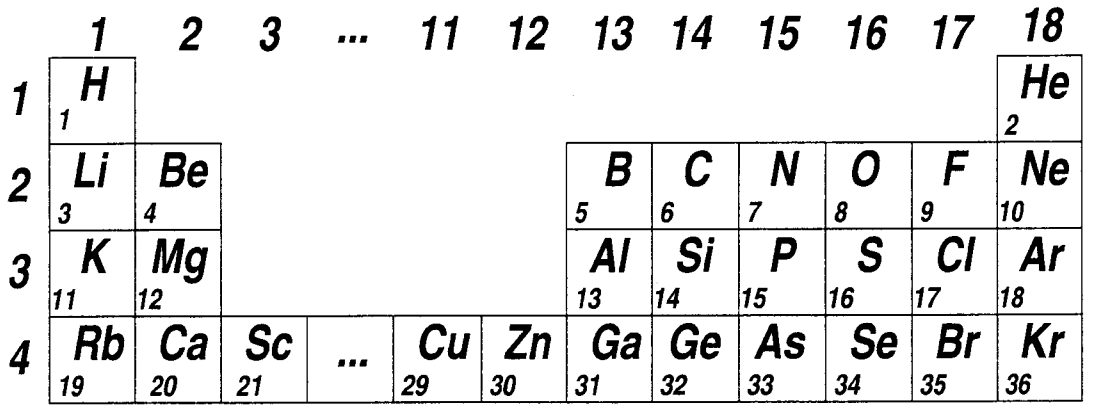

Figure 8. *The first four periods of the periodic table.*

The last element in such a period is generally a noble gas. The noble gases have electron orbits filling their outer shells. This means that the energy to ionize one of the outer electrons is relatively large with respect to other atomic elements. However, molecules involving the high atomic number noble gases are not unknown.

Since the structure of a typical noble gas will satisfy the condition that the outer shell is completely filled with electrons, it will not attract new electrons into the next outer shell. According to Gauss's theorem, the integral of the electric flux through a sphere which contains neutral charge is zero.

$$\int_{S^2(r)} \mathbf{E} \cdot \hat{\mathbf{dS}} = \int_{V(r)} \nabla \cdot \mathbf{E} \, dV = 0,$$

where $Q = 0$ is the total enclosed charge. But this result assumes that the charge distribution of positive and negatives charges in the sphere is homogeneous. This may not be the case in general, and in particular, the negative charge in the outer electron shells of neighboring atoms will act to separate the atoms, as a general rule. Hence, the theorem for atomic structures will depend, at comparatively small radii, on the wave distributions of the electrons most especially in the outer shells. If the atomic structure of noble gases most closely approximates the case of homogeneous charge distributions then one would expect that such atoms would have inert properties.

In summary, for ionic bonding, one atomic structure must have an electron wave distribution in the outer shell which will attract weakly bound electrons from another atom. If a weakly bound electron is more readily attached to one atom, then it will appear as a

cation and the other atom will appear as an anion. Coulomb forces will then act to bind the atoms into a molecular structure.

An example of ionic bonding is given by the sodium-chloride molecule. In this case, the metallic sodium becomes an anion and the nonmetallic chlorine becomes a cation.

Covalent bonding in a molecule is another example of a chemical bond. In the case of covalent bonding, two nonmetallic atoms typically share a pair of electrons or a set of electrons. By sharing electrons the two atoms combine into a lower combined energy state. The term valence electron refers to an electron that is bound to a particular atom. Covalence electrons are then shared electrons between at least two atoms.

An example of covalent bonding is the deuterium molecule with two hydrogen atoms.

Metallic bonding occurs in combinations of metallic atoms. Loosely bound electrons act as free electrons, i.e., can move freely from one atomic shell to another under small electromotive forces. Metallic bounding often occurs in lattice structures which is of less interest in our development here.

6. Intermolecular Van der Waals and London Forces

Consider two charge neutral molecules. The interaction energy between the two molecules is defined by the following first order approximation [5],

$$U = -\frac{\mu_I \mu_{II}}{R^3}(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2)),$$

where μ_I, μ_{II} are the dipole moments of the respective molecules and $\phi_1 - \phi_2$, represents the polar coordinate orientation of the dipoles (N.B. the energy is is maximized for $\phi_1 - \phi_2 = \pi$) of the respective molecules in polar coordinates, with the polar axis defined as a line that adjoins the center of the two molecules separated by a distance R. The interactions of the dipoles of the molecules can either be attractive or repulsive. The type of interaction is dependent on the orientation of the dipoles of the respective molecules. Statistically, if all possible orientations of the dipoles had an equal chance of occurring, then the average of the dipole moment of the system, μ would be zero.

To see this observe that

$$\int_0^{\pi}\int_0^{2\pi} \frac{\mu_I \mu_{II}}{R^3}\Big(2\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1)\sin(\theta_2)\cos(\theta_1 - \theta_2)\Big)\, d\theta_1\, d\phi_1 = 0,$$

since the integral of the sine function and the cosine function over a period is zero.

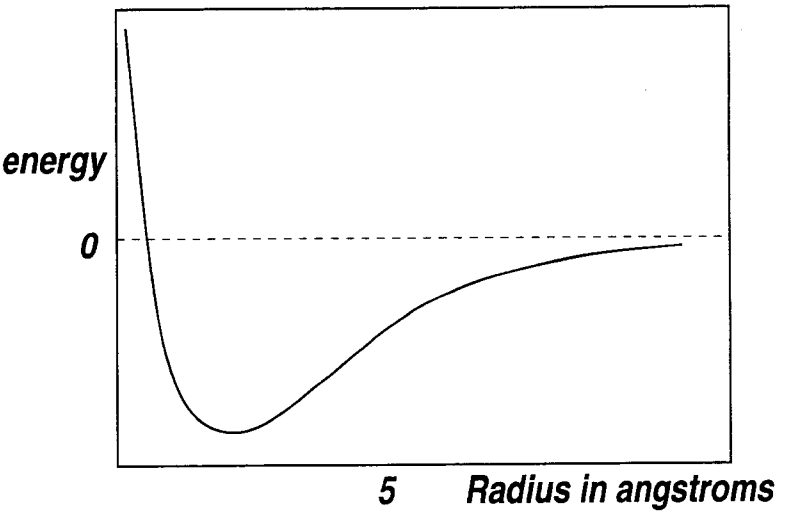

Figure 9. A typical average dipole interaction energy relation.

However, Boltzmann statistics dictate that dipole orientations with a lower energy level and thus lower temperature are preferred. Using the Boltzmann distribution, Keesom discovered the average interaction energy over all possible preferred orientations using Boltz-

mann statistics is given by

$$\tilde{U} = -\frac{2}{3}\frac{\mu_I^2\mu_{II}^2}{R^6}\frac{1}{\kappa T} \quad \text{for} \quad \frac{\mu_I\mu_{II}}{R^3} << \kappa T,$$

where κ is Boltzmann's constant and T is the temperature.

The most favorable orientation for the dipoles is an antiparallel along the line adjoining the molecules, which occurs when $\mu_1\mu_2/R^3 >> \kappa T$. Thus the average interaction energy for this statistical analysis is

$$\tilde{U} = -\frac{2\mu_I\mu_{II}}{R^3} \quad \text{for} \quad \frac{\mu_I\mu_{II}}{R^3} >> \kappa T,$$

which defines the lower limit for the interaction energy. The two afore mentioned energy functions induce the attractive force known as the orientation effect (cf. [5]).

The charge distribution of a molecule can be altered by the dipole moment of another molecule. The susceptibility of a molecule's charge distribution being effected by another molecules is known as the polarizability, which we denote as α. Consider a molecule with a specific polarizability, α placed in an external electric field $\vec{E}$. The external electric field will act on the molecule creating an induced dipole moment given by,

$$\vec{M} = \alpha\vec{E},$$

with the energy, U, which is the interaction energy of the induced dipole moment in the corresponding electric field $\vec{E}$,

$$U = \frac{-1}{2}\alpha E^2, \text{ where } E = |\vec{E}|.$$

Now that the induced dipole moment has been properly defined, consider the case with two molecules interacting with each other. Suppose that molecule I produces an electric field defined by

$$E_1 = \frac{\mu_I}{R^3}\sqrt{1 + 3\cos^2(\theta_1)}.$$

The energy of the induced dipole moment on molecule II by the electric field of molecule I polarizing molecule II is

$$U = \frac{-1}{2}\alpha_2 E_1^2 = \frac{-\alpha_2}{2}\frac{\mu_I^2}{R^6}(1 + 3\cos^2(\theta_1)).$$

The negative sign here means the interaction energy is attractive. Since this type of interaction is temperature independent, the interaction energy can remain attractive for infinitely

high temperatures. Taking $\cos^2\theta = 1/3$, the interaction energy between molecule I and molecule II becomes,

$$\tilde{U}_{I\to II} = -\alpha_2 \frac{\mu_I^2}{R^6}.$$

Once the charge distribution of molecule II changes due to the induced dipole moment from molecule I, molecule II then induces a dipole moment on molecule I. Thus the total interaction energy between the molecules is given by,

$$\tilde{U} = -\frac{1}{R^6}(\alpha_1\mu_{II}^2 + \alpha_2\mu_I^2).$$

Generally, if the molecules are the same, then the total interaction energy of the molecules from the action of induced dipole moments is

$$\tilde{U} = -\frac{2\alpha\mu^2}{R^6}$$

which is known as the induction effect.

Now consider two spherically symmetric systems each composed of a three-dimensional isotropic harmonic oscillators with charge e, such that there is no permanent dipole moment when they are at rest and both have a polarizability, α. Let the two systems be artificially perturbed, such that they are displaced from rest, where the displacements are respectively given by,

$$\vec{r_1} = (x_1, y_1, z_1) \quad \text{and} \quad \vec{r_2} = (x_2, y_2, z_2).$$

From the displacement vectors the potential energy of the interaction systems is,

$$V = \frac{e^2 r_1^2}{2\alpha} + \frac{e^2 r_2^2}{2\alpha} + \frac{e^2}{R^3}(x_1x_2 + y_1y_2 + z_1z_2),$$

where the first two terms represent the total elastic energy of the system and the second term represent the dipole interaction energy. If the two systems where in equilibrium, i.e., $(x_1 = x_2 = \cdots = z_2 = 0)$, then classically the systems would not interact with each other when place within a distance, $R > \sqrt[3]{2\alpha}$.

From the perspective of quantum mechanics, the oscillators will never be in a true classical equilibrium due to the zero-point energy property. Redefining the displacement vectors of the system we have

$$x_\pm = x_1 \pm x_2; \quad y_\pm = y_1 \pm y_2; \quad z_\pm = z_1 \pm z_2,$$

$$\vec{r}_+ =< x_+, y_+, z_+ > \quad and \quad \vec{r}_- =< x_-, y_-, z_- >$$

This allows the potential energy of the system to be defined as,

$$V = \frac{e^2}{2\alpha}(r_+^2 + r_-^2) + \frac{e^2}{2R^3}(x_+^2 + y_+^2 - 2z_+^2 - x_-^2 - y_-^2 + 2z_-^2)$$

$$= \frac{e^2}{2\alpha}\Big[\left(1 + \frac{\alpha}{R^3}\right)(x_+^2 + y_+^2) + \left(1 - \frac{\alpha}{R^3}\right)(x_-^2 + y_-^2) + \left(1 - 2\frac{\alpha}{R^3}\right)z_+^2 + \left(1 + 2\frac{\alpha}{R^3}\right)z_-^2\Big].$$

Furthermore, the frequencies of the oscillators are defined as,

$$\nu_x^{\pm} = \nu_y^{\pm} = \nu_0\sqrt{1 \pm \frac{\alpha}{R^3}} \approx v_0\left(1 \pm \frac{\alpha}{2R^3} + \frac{\alpha^2}{8R^6}\right)$$

and

$$\nu_z^{\pm} = \nu_0\sqrt{1 \mp \frac{2\alpha}{R^3}} \approx v_0\left(1 \mp \frac{\alpha}{R^3} + \frac{\alpha^2}{2R^6}\right),$$

where $\nu_0 = e/\sqrt{m\alpha}$ is known as the proper frequency of the systems and where the approximation is obtained from the binomial expansion theorem

$$\sqrt{1+x} = 1 = \frac{x}{2} + \frac{x^2}{8} + \cdots$$

and is valid only for α/R^3 sufficiently small.

The lowest energy state of the system can now be found by using the definition of the zero point energy,

$$U_0 = \frac{1}{2}h\nu,$$

where h is Planck's constant. Thus the lowest energy state of the system is,

$$U_0 = \frac{h}{2}(\nu_x^+ + \nu_y^+ + \nu_z^+ + \nu_x^- + \nu_y^- + \nu_z^-)$$

$$= \frac{h\nu_0}{2}\left[6 + \left(\frac{1}{2} + \frac{1}{2} - 1 - \frac{1}{2} - \frac{1}{2} + 1\right)\frac{\alpha}{R^3} + \left(\frac{4}{8} + \frac{2}{2}\right)\frac{\alpha^2}{R^6} + \cdots\right]$$

$$\approx 3h\nu_0 + \frac{3}{4}\frac{h\nu_0\alpha^2}{R^6}.$$

The first term represents the total zero point energy of the systems and the second term represents the attractive interaction energy of the systems. This implies that there is an attractive force which in part characterizes the Van der Waals force.

7. The Casimir Effect

In 1947, J. Overbeek discussed an unusual observed phenomenon in colloidal chemistry with H.B.G. Casimir and D. Polder attempted to discover the mathematical theory behind the phenomenon and subsequently published, *The Influence of Retardation on the London-van der Waals Forces* [1], applying principles of quantum mechanics. Afterward, Casimir consulted N. Bohr concerning this effect. Using Borh's advice concerning the zero point energy hypothesis, Casimir then published a short paper, *On the attraction between two perfectly conducting plates* [2], extending the results to a force between two perfectly conducting plates. This produced a new theory that was later named in Casimir's honor. The Casimir effect had been regarded as little more than a novelty in physics until it was experimentally verified and measured in 1997, by S.K. Lamoreaux [4]. In fact, the Casimir effect has since been observed to play a profound role in several branches of physics. In order to better understand this important advance in physics, it is important to understand its beginnings which we summarize here.

As we have seen the theoretical mechanics behind the Casimir effect was initiated by the work of one of the founders of quantum physics, Max Planck. In particular, quantum mechanics developed in order to understand the properties of blackbody radiation. A precise measurement of the radiation over a multitude of temperatures, investigated by Heinrich Rubens and Ferdnand Kurlbaum, revealed that the Wein/Rayleigh-Jeans distribution laws could not adequately model the observable radiation distribution from a blackbody. Using the data from Ruben's and Kurlbaum's measurement Planck was able to determine a better distribution law. Namely,

$$U = \frac{h\nu}{2\pi[\exp(h\nu/2\pi\kappa T) - 1]},$$

T is the absolute temperature of the black body and ν is the frequency of the oscillator. Planck set out to refine and explain the reason that the distribution assumed this form. To do this, Planck crafted a thought experiment that would lead to the first hypothesis of quantum physics.

Planck began his thought experiment by envisioning a closed cavity composed of walls that were perfectly reflective. He then placed n oscillators with defined frequencies

$$\{v_1, v_2, \ldots, v_n\}$$

in the cavity. Since the total energy of the system is composed of the sum of the vibrational

energy of the oscillators and the radiation energy, Planck wanted to distribute the energy of the system over all the oscillators so the oscillators would all have the same frequency. In classical theory, the energy of the system can be distributed in infinite combinations over the oscillators in the cavity, since the energy is infinitely divisible. Planck instead thought of the energy of the system as being defined as a set of finite and equal parts. The theory required a natural constant, which was initially assigned the value

$$h = 6.55 \times 10^{-27} \text{erg} \cdot \text{sec}$$

obtained by empirical calculations and later named in Planck's honor (the current approximation is $h = 6.62 \times 10^{-27}$erg sec). The constant was related to the energy of the oscillators. By multiplying the frequency of the oscillators, v by h and dividing the total energy of the system U by hv he was able to find the number of *energy elements* or what Planck referred to as quanta that where distributed over a system composed of n oscillators. Thus the first quantum hypothesis is given: energy must be quantized into discrete integer packets.

Planck's hypothesis was met with skepticism, mainly from traditional physicists. This concerned Planck as he had never intended to replace or disprove the principles of classical physics. Quite the contrary, Planck was seeking a way to augment classical physics. At this time there were still gaps in classical electromagnetic theory for radiation propagation through space. Planck wanted to use his original hypothesis to show that not only was it founded in classical physics, but that his hypothesis explained phenomenon that classical physics could not. This lead Planck to his second quantum hypothesis.

The problem that Planck had with his original model involved the fact that a finite amount of quanta, from a finite amount of radiation, will take a finite amount of time to be absorbed by matter. The total time is dependent on the intensity of the radiation. The weaker the radiant source, the more time that will be needed for the energy to be absorbed. When Planck applied this to his model he found that for a given temperature, as the frequency of the radiation increases, the energy of the radiation increases and the radiation intensity decreases rapidly. Thus his model showed that as the frequency of the radiation increases the amount of time needed to absorb the radiation would become very large. To resolve this issue, Planck needed modify his original hypothesis.

Planck assumed that the absorption of radiation would proceed at a continuous rate, which would allow for the oscillators of the system to be continuously variable, thus taking

any value from 0 to ∞, which follows from classical electrodynamics. By his original hypothesis, the oscillators can only emit energy in the form of quanta, when the energy of the oscillator becomes a whole multiple of Planck's constant and the frequency of the oscillator satisfies

$$\Delta U = nh\nu,$$

where $n \in \mathbb{Z}^+$. However, the emission of quanta from an oscillator is completely stochastic.

Planck's original hypothesis assumed that if an emission does occur, the oscillator loses all of its energy, to the emitted radiation. During the time between emissions of quanta an oscillator is increasing its energy by continuously absorbing radiation, with the total amount of radiation absorbed being proportional to the interval of time over which the absorption occurred. This suggests a relationship between the absorption of radiation by discrete quanta and emission of radiation by discrete quanta from an oscillator. In other words, the energy of the emitted quanta would be be equal to the sum of the energy of all the absorbed radiation by the oscillator before that emission occurred. With this relationship Planck effectively reduced his hypothesis to a classical physics problem.

Planck then sought an explanation to the interaction of quanta with oscillators that would be compatible with the current classical models, e.g., the Wien and the Rayleigh-Jeans distribution laws. However, his improved distribution law came in a distinctly non-classical form, namely the added zero-point energy term. Planck's original distribution law was modified as,

$$\Delta U = \frac{h\nu}{4\pi}\frac{\exp(h\nu/2\pi\kappa T)+1}{\exp(h\nu/2\pi\kappa T)-1} = \frac{h\nu}{4\pi} + \frac{h\nu}{2\pi[\exp(h\nu/2\pi\kappa T)-1]}.$$

Here the additional term is $h\nu/4\pi$ and it gives the zero-point energy of the system. When $T = 0°K$, then the zero-point energy of the oscillator is known as the rest energy of the system. The zero point energy does not interfere with the laws that govern blackbody radiation. Furthermore, the energy of the oscillator agrees with the classical Rayleigh-Jeans distribution law at high temperatures and long wavelengths. Thus Planck had succeeded in developing a distribution law that is founded in and agrees with classical physics at the macroscopic level.

We now turn to the question of the Casimir effect. Work on the Casimir effect was initiated by an observation made by J. Overbeek in the 1940s. At the time, Overbeek and Verwey [7] were studying the properties of quartz powder in suspension at Philips Labo-

ratory in Einhoven, Netherlands. It was during these experiments that Overbeek observed that the theory of colloidal stability, which he had developed in conjunction with Verwey, was flawed. Overbeek surmised that the disparity between his theory and experimental observation might be corrected if interaction of the particles of the suspension decreased rapidly at larger distances than his original supposition allowed.

Overbeek thought that the disparity might have been due to the fact that the speed of light is finite and he shared this thought with Casimir and Polder, both of whom were employed at Philips Laboratory at the time. Overbeek's suggestion encouraged Casimir and Polder to consider the theory of colloidal stability with the retarded van der Waals force interaction included. Once they included the retarded van der Waals forces in the theory, they posited that the Overbeek was correct. Adding the retardation forces to the theory yielded that the intermolecular particle interaction varied inversely as R^7 rather than as R^6, for large intermolecular distances. Casimir was intrigued by this result and decided to study the phenomena further.

In order to seek a better understanding of what Casimir and Polder had derived, Casimir discussed the results with Niels Bohr during a walk. Bohr suggested that Casimir might want to consider his computations assuming the interactions at zero point energy. The pursuit of Bohrs suggestion led to the discovery of the Casimir effect.

The Casimir effect is a very complex entity. While is has its beginnings in the Van der Waals forces, in reality it is an artifact of a macroscopic quantum field theory.

Van der Waals forces result from the interaction of dipole moments of atoms. When the moment of a dipole of an atom changes instantaneously, this change effects the dipoles of atoms neighboring the effected atom. These changes are brought about by the original dipole changing its orientation which causes its neighboring atoms dipoles to reorient themselves to the new position of the original dipole as we have already seen. The dipoles of neighboring atoms change due to the instantaneous dipole of the original atom producing an oscillating electric field that then acts on the polarizability of a neighboring atoms to change their orientation.

F. London [4] called the sum of these interactions the dispersion effect. To better explain the dispersion effect consider two atoms of a gas in a vacuum. Call them atom A and atom B. Suppose atom B experiences an instantaneous dipole moment. The instantaneous dipole on atom B induces a dipole on atom A which causes atom A to move in phase with atom

B. Thus producing an attractive interaction between atom A and atom B.

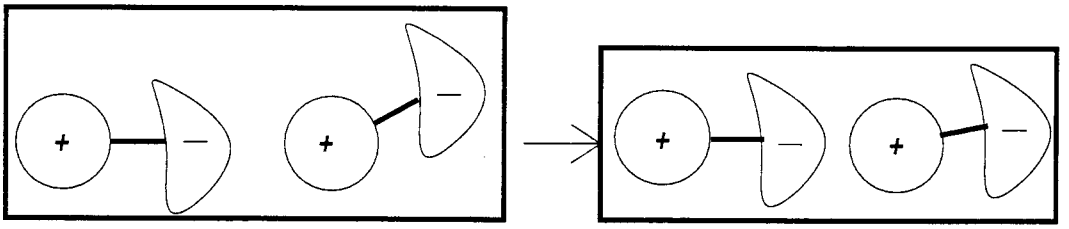

Figure 10. The alignment of a pair of dipoles.

London determined that the energy of the interaction between any two atoms (i, j) is defined by

$$U = -\frac{\lambda_{i,j}}{R^6},$$

where $\lambda_{i,j}$ is known as London's constant and R is the distance separating the two atoms. The London constant is an empirical value which is partially dependent on the atomic numbers of the interacting atoms. London's formula for U is only valid over distances that are smaller than the wavelength of the major electronic absorption bands for the specific gas in question. For greater distances a new effect becomes apparent. That effect is known as the Retardation effect.

The Retardation effect's energy is inversely proportional to R^7 and the effect produces an attraction interaction between any two atoms. If the distance separating any two atoms is greater than the wavelength of the major electronic absorption band for a specific gas, on the order of about 10 nanometers, then the electric field produced by the induced dipole has a reduced effect on the atom that originally caused the induced dipole. This causes the neighboring atoms that where previously in-phase with the atom that originally had the induced dipole, to change their orientation and move out of phase.

As the atoms move out of phase with the original dipole, the induced dipole's electric field becomes less effective. Thus reducing the energy of the interaction (cf. [5]).

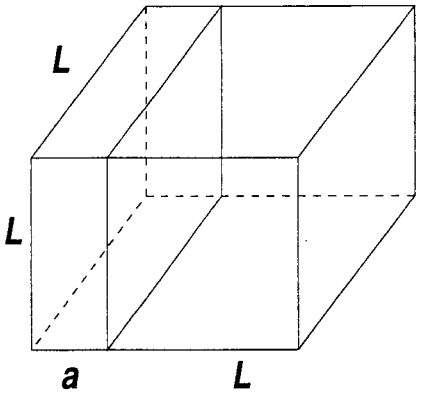

Figure 11. The variation of the distance between two metal plates.

Consider the space in a perfectly conducting box with the dimensions $L \times L \times L$. According to theory, the tangential component of the electric field tangent to the perfectly conducting plates must vanish. Therefore, the eigenstates of the electromagnetic field in the enclosed space of the box derived from Maxwell's equations are of the form [1],

$$E_{x,j,\mathbf{k}} = c_{x,j,\mathbf{k}} \cos(\frac{k_1 \pi x}{L}) \sin(\frac{k_2 \pi y}{L}) \sin(\frac{k_3 \pi z}{L}),$$

with similar formulations for y and z. Here we take $\mathbf{k} =< k_1/\pi/L, k_2\pi/L, k_3\pi/L >$ for $k_1, k_2, k_3 \in \mathbb{Z}^+$, and

$$\mathbf{e}_{j,\mathbf{k}} =< e_x(j,\mathbf{k}), e_y(j,\mathbf{k}), e_z(j,\mathbf{k}) >$$

is the unit vector perpendicular to the wave vector $\mathbf{k}$ which represents the polarization vectors indicated by $j \in \{1,2\}$. Then the vector component can be written as

$$\mathbf{E}_{j,\mathbf{k}} = \sum_{j,\mathbf{k}} < E_{x,j,\mathbf{k}} e_x(j,\mathbf{k}), E_{y,j,\mathbf{k}} e_y(j,\mathbf{k}), E_{z,j,\mathbf{k}} e_z(j,\mathbf{k}) > .$$

The vector potential of the field inside the box is given by

$$\mathbf{A} = \sum_{\mathbf{k},j} (A_{j,k} e^{-i\omega_k t} + A^\dagger_{j,k} e^{i\omega_k t}) \mathbf{E}_{j,\mathbf{k}}.$$

Here $A_{j,k}$ is a 3×3 matrix, and $A^\dagger_{k,j}$ is the adjoint of $A_{k,j}$. Using the vector potentials it is possible to determine the energy of the electromagnetic field in the box,

$$U = \frac{1}{4\pi} \int E^2 dy = \frac{L^3}{4\pi} \sum_{j,k} \frac{hc}{L^3} k (A^\dagger_{j,k} A_{j,k} + A_{j,k} A^\dagger_{j,k})$$

$$= \sum_{k,j} \frac{h\omega_{\mathbf{k}}}{4\pi} (A^\dagger_{j,k} A_{j,k} + A_{j,k} A^\dagger_{j,k}).$$

Observe that the time independent condition on the components of the electric field imply that we have standing waves such that the wave length divides the length L and $\omega_{\mathbf{k}}$ is the corresponding angular velocity for the given wave component. The question is whether or not the entire Fourier representation of the electric field will apply when the distance between the metal plates is small in comparison to some of the wavelengths which appear in a portion of this Fourier representation.

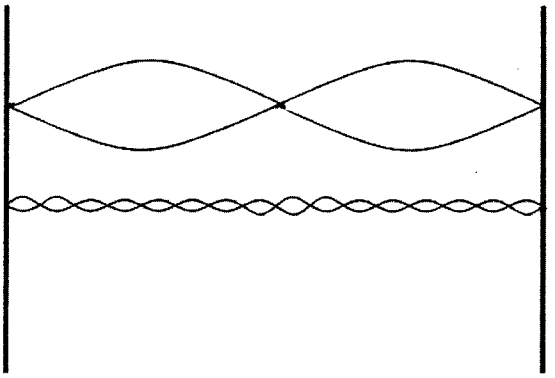

Figure 12. Examples of standing Fourier waves in the z direction.

Since the summation is the result of a Fourier expansion, the index is taken over a countably infinite set. In many cases this energy value is taken to be infinite because the potential energy function is modeled on the inverse square law. Consider the work integral

$$W = \int_o^1 \frac{K}{r} dr = K \lim_{b \to 0} \ln(\frac{1}{b}),$$

which is clearly undefined. In actuality, the potential function is not infinite for a set of facing metal plates. To see this we need only consider the concept of pressure welding two metal plates. We have ignored the question of heating the surface into a plastic state. The point is that while there is an electric field induced by the Coulomb potentials, we will assume in our development that the total energy in a vacuum at zero temperature is finite. We, therefore, avoid the standard assumption of an infinite energy induced by the field which is then is remedied in the final result by subtracting out the common infinite potential at the surface boundaries for two distinct fields, E_I and E_{II}, to obtain a finite difference in the energies.

The assumption of the zero energy state allows us to ignore the energies associated to vibrations in the metals. In addition, it is assumed that there is no background radiation interference.

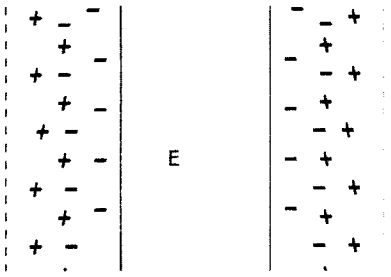

Figure 13. Dominant Coulomb forces on the outer free electron layers of two metal plates.

Casimir and Polder showed that the interaction of an ideal conducting plate and a neutral atom or molecule with a defined static polarizebility given by α is limited by a distance R defined by following relation,

$$\Delta U = \frac{3hc\alpha}{16\pi^2 R^4}.$$

The relation was obtained by modifying the Van Der Waals-London force to account for the retardation effect on dipoles. However, the function ΔU can also be determined by studying electromagnetic zero point energy.

Consider a cube, with walls made of a perfectly conducting material, that forms a cavity with a volume of L^3. Now place a perfectly conducting plate, with an area of L^2 in the cavity such that it is parallel to the one of the sides of the cavity. Now allow the parallel plate to vary in distance from one of the walls of the cavity from nearly touching the wall to a maximum distance from the wall of $L/2$. The expression

$$\frac{1}{2}\sum_a \frac{h}{2\pi}\omega_a,$$

where ω_a is a resonance frequency of the cavity at a specific plate separation. This expression results in a divergent sum that lacks any physical significance. However, the difference between the expression given a the least distance between the plates and expression given at the maximum distance between the plates, $L/2$, denoted

$$\frac{1}{2}\left(\sum_a \frac{h}{2\pi}\omega_a\right)_{L/2} - \frac{1}{2}\left(\sum_b \frac{h}{2\pi}\omega_b\right),$$

is well defined and represents the interaction of the wall of the cavity with the movable parallel plate. After Casimir came to this conclusion he set out to quantify the interaction of the plates. To accomplish this Casimir redefined the parameters of his thought experiment.

Casimir began by parametrizing the vibrations of the cavity. He defined the cavity to be,

$$0 \leq x \leq a, 0 \leq y \leq L, 0 \leq z \leq L,$$

where d is the distance between the wall of cavity and the moveable parallel plate.

Casimir could then associate the following wave numbers to the define the vibrations in the cavity,

$$n_x = \frac{\pi}{a}k_1, n_y = \frac{\pi}{L}k_2, n_z = \frac{\pi}{L}k_3,$$

where $k_1, k_2, k_3 \in \mathbb{Z}^+$. Thus Casimir defined the wave vector of the vibrations in the cavity,

$$\mathbf{k} = \sqrt{n_x^2 + n_y^2 + n_z^2} = \sqrt{n_x^2 + r^2},$$

where $r = \sqrt{n_y^2 + n_z^2}$ and $n_y = r\cos(\theta)$. Every component of the wave vector, i.e. n_x, n_y, n_z has two standing waves that correspond to them unless one of the components k_i value is zero. In that case one standing wave corresponds to each wave vector component. Casimir goes onto surmise that since L can be considered large relative to d that the importance of the standing waves in regards too the wave vector components n_y, and n_z is not worth consideration. He thus considers n_y and n_z to be continuous variables, with this assumption Casimir redefined the expression of the resonance frequencies in the cavity in terms of the wave vector components up to some value N,

$$\omega_a = \frac{cL^2}{\pi^2}\Big[\frac{1}{2}\sqrt{n_y^2 + n_z^2} + \sum_{n=1}^{N}\sqrt{n^2\frac{\pi^2}{a^2} + n_y^2 + n_z^2}\Big].$$

Define

$$U_{N,\rho} = \frac{1}{2}\sum_a \frac{h}{2\pi}\omega_a = \frac{h}{2\pi}\frac{cL^2}{\pi^2}\int_0^{\rho}\int_0^{\sqrt{\rho^2 - n_z^2}}\left[\frac{1}{2}\sqrt{n_y^2 + n_z^2} + \sum_{n=1}^{N}\sqrt{n^2\frac{\pi^2}{a^2} + n_y^2 + n_z^2}\right] dn_y dn_z.$$

$$= \frac{h}{2\pi}\frac{cL^2}{\pi^2}\cdot\frac{\pi}{2}\int_0^{\rho}\Big[\frac{r}{2} + \sum_{n=1}^{N}\sqrt{n^2\frac{\pi^2}{a^2} + r^2}\Big]\ r\ dr,$$

$$= \frac{hcL^2}{8\pi^2}\Big[\frac{\rho^3}{3} + \sum_{n=1}^{N}\Big(n^2\frac{\pi^2}{a^2} + \rho^2\Big)^{3/2} - \Big(\frac{n\pi}{a}\Big)^{3/2}\Big].$$

where the integral for θ is over the interval $0 \leq \theta \leq \pi/2$ and ρ must go to infinity to include all wave components.

By subtracting the energy of the waves that have a wavelength longer than the separation distance of the plates a, Casimir arrived at the total energy of interaction between the plates,

$$\Delta U_{N,\rho} = \Big[U_{N,\rho} - \frac{hcL^2}{4\pi^2}\int_0^N\int_0^{\rho}\sqrt{\frac{n^2\pi^2}{a^2} + r^2}\ r\ drdn\Big],$$

or

$$\Delta U_{N,\rho} = \Big[U_{N,\rho} - \frac{hcL^2}{4\pi^2}\int_0^{\pi N/a}\int_0^{\rho}\frac{a}{\pi}\sqrt{n_x^2+r^2}\; r\; dr dn_x\Big].$$

Essentially, the idea is that the cavity is acting like a wave mode filter. The longer wavelengths do not produce a standing wave in the cavity are thereby removed from the total energy evaluation. The wavelengths shorter than the separation distance, a, of the plates may contribute to the total energy. Consequently the variation in the energy is due to the difference in the allowed wavelengths.

To refine the results and further filter out long wavelength waves, Casimir multiplied the integrands by the function $f\,(n/n_m)$, where

$$f\Big(\frac{n}{n_m}\Big) = \begin{cases} 1 & : \quad n/n_m << 1 \\ \frac{1}{2} & : \quad n = n_m \\ 0 & : \quad n/n_m >> 1 \end{cases}$$

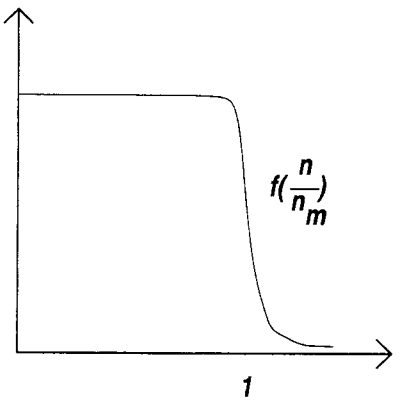

Figure 14. An example of the function $f(n/n_m)$.

The physics behind this dictates that for extremely short wavelengths, i.e., on the order of x-rays and gamma rays, the plates that compose the cavity are virtually transparent and thus the energy interaction calculation will not be influenced by these waves. To simplify the integrals further, Casimir introduced the change of variable $u = a^2r^2/\pi^2$. Thus the interaction energy becomes,

$$\Delta U_{N,\rho} = \lim_{\rho\to\infty} L^2\frac{hc\pi}{8a^3}\Big[\sqrt{\frac{u}{4}}+\sum_{n=1}^{N}\int_0^{a^2\rho^2/\pi^2}\sqrt{n^2+u}\; f\Big(\pi\sqrt{n^2+\frac{u}{an_m}}\;\Big)\,du$$

$$-\int_0^{N}\int_0^{a^2\rho^2/\pi^2}\sqrt{n^2+u}\; f\Big(\pi\sqrt{n^2+\frac{u}{an_m}}\Big)\,du\,dn)\Big].$$

We applying another change of variable $w = u + n^2$, and consider the function defined by,

$$F(n) = \int_{n^2}^{\infty} w^{\frac{1}{2}} f\Big(\frac{w\pi}{an_m}\Big) dw.$$

This definition will allow us to evaluate the tail of the integral for ΔU in each case.

Casimir then applied the Euler-Maclaurin formula to obtain,

$$\frac{1}{2}F(0) + \sum_{n=1}^{\infty} F(n) - \int_0^{\infty} F(n)dn = (-\frac{1}{12}F'(0) + \frac{1}{24 \times 30}F'''(0) + \cdots).$$

Using the Fundamental Lemma of Calculus, we may easily compute the derivatives

$$F'(0) = 0; \quad F'(n) = -2n^2 f(\frac{n^2\pi}{an_m}); \quad F''(0) = 0; \quad F'''(0) = -4.$$

Observe that for large n the the contribution of the integral can be taken to be zero. Using the first non-zero term in the series, Casmir deduced that the interaction energy per area is

$$\frac{|\Delta U|}{L^2} = \frac{hc\pi \times 4}{8 \times 24 \times 30} \cdot \frac{1}{a^3}.$$

From this fact he then determined that the force per unit area could be written as,

$$F = \frac{hc\pi}{480}\frac{1}{a^4} = 0.013\frac{1}{a^4}\frac{dyne}{cm^2},$$

with the plate separation distance a measured in microns.

From this Casimir concluded that an attractive force will exist in the cavity of any parallel plates, regardless of the material the plates are made of, due to the modes of the wavelengths in the cavity. This force is the result of the physical manifestations i.e pressure of the zero point energy of the electromagnetic waves.

A similar question may be asked with respect to dipole fields between neutral atoms suspended in a liquid. This is the effect which Overbeek and Verwey noticed in their experiments in colloidal chemistry.

8. Measurement of the Casimir Force

The Casimir effect was verified by S.K. Lamoreaux in his paper, *Demonstration of the Casimir Force in the 0.6 to 6 μm Range* [4] in 1997. In Casimir's original thought experiment he used parallel plates to create the cavity that generates the effect. However, Lamoreaux chose to use a flat plate and a sphere for his measurement of the Casimir force, after his initial attempt to product the effect failed. Lamoreaux's initial attempt failed because of the difficulty keeping the flat plates perfectly parallel. Lamoreaux's choice to use a flat plate and a sphere solved this problem, as any point on the surface of the sphere is always tangent to the flat plate. Thus the plate always remains parallel to a point on the sphere. Lamoreaux then modified Casimir's original expression of the Casimir force to compensate for replacing one of the flat plates with a sphere. Thus Casimir's original expression,

$$F(a) = \frac{\pi}{480}\frac{hc}{a^4}A,$$

becomes

$$F_c(a) = R\left(\frac{1}{3}\frac{\pi^2}{240}\frac{hc}{a^3}\right),$$

where R is the radius of curvature, c is the speed of light, h is Planck's constant , $A = 2\pi aR/3$ is the area of the flat plates, and a is the length of the cavity. Lamoreaux then made two corrections to this force expression to account for certain experimental anomalies.

The first correction is due to the temperature at which the measurement was occurred, $T \approx 300^oK$. This thermal correction is different for both the Casimir and van der Waals forces. The energy of the surface of the of the plates is given by

$$U = aU^{00},$$

where U^{00} is the energy density.

The appropriate modification of the force due to this temperature effect is made using the Proximity Force Theorem (PFT), which defines the force between two slightly curved surfaces, as a function of the degree of freedom of separation of the interacting surfaces denoted by s proportional to the interaction potential of the surface area denoted by $e(s)$. In this case the PFT simplifies to

$$F = 2\pi RE,$$

where R is the radius of curvature of the spherical plate and E is the interaction potential per unit surface area of the plates, which results in a attractive force between the plates.

Thus, the Casimir force becomes

$$F_c^T(a) = F_c(a)\left(1 + \frac{720}{\pi^2} f(\xi)\right),$$

where $\xi = \frac{kTa}{\hbar c} = 0.126 a\mu m^{-1} a T = 300°K$. and the function f is given by

$$f(\xi) = \begin{cases} \frac{\xi^3}{2\pi}\zeta(3) - \frac{\xi^4\pi}{45}, & \text{for } \xi \leq \frac{1}{2}, \\ \frac{\xi}{8\pi}\zeta(3) - \frac{\pi^2}{720} & \text{for } \xi > \frac{1}{2}. \end{cases}$$

Here $\zeta(3) = 1.202$. This correction begins to exhibit characteristics of a classical effect as it becomes independent of $hc/2\pi$ and follows the Rayleigh-Jeans limit for a black body at large values of a.

The second correction is due to the conductivity of the plates. Again modifying this force by the PFT and modifying $F_c(a)$, yields

$$F_c' = F_c(a)\left(1 + \frac{4c}{a\omega_p}\right),$$

where ω_p represents the plasma frequency of the conductor with an effective electric susceptibility of $\epsilon(\omega) = 1 - (\omega_p/\omega)^2$.

With Casimir's original force equation corrected to account for experimental anomalies, Lamoreaux measured the Casimir force with an accuracy of about 5% error.

9. Conclusion

The Casimir effect had remained an obscure footnote in the annals of physics since its discovery in 1948. Then in the late 1990's it ignited a renaissance in physics. The effect changed the perspective of many physicists about zero point energy. The effect showed that a force could be produced by the vacuum energy of a system. "A force from nothing," as most physicists put it, which despite its obvious philosophical meaning, is extremely intriguing. Especially, when the simplicity of the concept and derivation of the effect is taken into consideration.

As we have seen, the Casimir effect is the result of limiting the electromagnetic modes in the cavity created by two conducting plates. The energy of the modes can be expressed as

$$\frac{1}{2}\sum_a \frac{h}{2\pi}\omega_a e^{-i\omega_a\tau} = \frac{h}{4\pi}\int_{-\infty}^{\infty} e^{-I\omega\tau}\sum_a \frac{2\omega}{\omega_a^2-\omega^2-i\epsilon}\frac{d\omega}{2\pi i}, \tau \to 0,$$

where a represents the modes, and ω_a is the frequency of the wave inside the cavity (cf. [7]). The action of the zero-point energy contained in the cavity generates an attractive force on the plates. Literally, the vacuum energy of cavity is causing the plates to be drawn to one another. Thus, seemingly producing a force from nothing.

The Casimir effect is becoming an important subject beyond physics. However, it is still profoundly important to the field of physics, especially Quantum Field Theory, Cosmology and Mathematical Physics. In Quantum Field Theory, the effect allows for spontaneous physical compactification of extra spatial dimensions and is important to emerging physics such as super - gravity and symmetry, and string theory. In Cosmology, the effect can occur in space-times that have a non-trivial topology. In fact the vacuum polarization that results from the effect may be the cause to the inflationary process of the Universe. Finally, in Mathematical Physics, the study of the effect has generated regularization and renormalization methods based on zeta functions and the heat kernel expansion. It took almost 50 years for the Casimir effect to become mainstream, only time will illuminate the further development of this extraordinary effect.

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